Thick Nano-Structured CVD Coating HARDIDE as Enabler for Engineering Systems in Extreme Wear and Erosion Conditions.

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Thick Nano-Structured CVD Coating HARDIDE as Enabler for Engineering Systems in Extreme Wear and Erosion Conditions.

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1. Abstract

Hardide™ is a new family of low-temperature CVD (Chemical Vapour Deposition) Tungsten/Tungsten Carbide coatings. Hardide-T type coating consists of Tungsten Carbide nano-particles dispersed in a metal Tungsten matrix which gives the material enhanced hardness of between 1100 and 1600 Hv, and abrasion resistance up to 12 times better than Hard Chrome. The coating can be produced on stainless steel, some tool steels, Ni-, Co- and Cu-based alloys with a controllable coating thickness ranging from 5 to 100 microns; unique for hard CVD coatings. As a nano-structured material, it demonstrates outstanding toughness, crack and impact resistance by withstanding 3000 microstrain deformations without any damage; this deformation will crack or chip any other thick hard coating.

The gas-phase CVD process enables coating internal surfaces and complex designs such as dies, moulds and pump cylinders. The coating is resistant to acids and aggressive media; its resistance to H_2S is proven by NACE testing.

Hardide-T is applied to coat critical components in high wear and/or aggressive media environments including oil and gas down-hole tools, pumps for abrasive and viscous fluids, valves and heavy-duty parts for earth moving equipment. Typically, the coating increases the life of precipitation hardened stainless steel parts in abrasive conditions by a factor of 3.

In several applications, Hardide has proven to be the solution which enables the feasibility of systems designed to operate in extreme wear and erosion conditions. One example is a valve design which involved significant seat deformation during closing. Hardide proved to be the only material which could withstand the deformation and protect the seat from wear and erosion.

Hardide is an attractive replacement for Hard Chrome, which is to be phased-out due to environmental considerations.

2. Introduction.

A number of hard coatings and surface treatments are successfully used to improve mechanical systems operation in severe abrasion service, among them HVOF spray coating, Hard Chrome and D-gun. Traditional PVD and CVD coatings help to reduce friction and Boron diffusion reduces galling. Meanwhile each of these surface engineering processes has its limitations; in particular the current PVD and CVD processes produce very thin coatings - typically less than 5 microns [1, 2, 3] - which cannot resist abrasive or erosive conditions, have low load-bearing capacity. Chrome plating is under pressure for environmental reasons and while HVOF spray coating is considered a possible alternative to Chrome, it is not suitable for internal surfaces and has porosity between 1% and 5% of the coating volume. Furthermore, most of these treatments are prone to cracking, negatively affect fatigue resistance and do not protect parts against aggressive media.

To address some of these shortcomings of currently used coatings a family of innovative CVD Tungsten/Tungsten Carbide coatings has been developed under the name Hardide®. Table 1 below presents the key characteristics of 3 types of Hardide coatings.

This article focuses on Hardide-T type coating which consists of nano-particles of Tungsten Carbide integrated in dense and pore-free alloyed Tungsten matrix. This coating offers an exceptional combination of properties and proven as enabling some of the critical components operation is highly abrasive and erosive environment [4, 6, 7].

The coating is produced by a low-temperature Chemical Vapour Deposition (CVD) process as a layer with a thickness between 5 and 100 microns on steel, including stainless steel, some tool steels, Ni-based and Co-based alloys. Pore-free Hardide-T is crystallised from gas-phase atom-by-atom, this enables the coating of internal and shaped “out of line-of-sight” surfaces, for example in a cylinder or bush.

Table 1: Types of Hardide coatings.

Type	Hardness	Toughness	Thickness	Applications
Hardide-T Tough	1100 – 1600 Hv	Excellent	Typically 50µm Up to 100 µm on some substrates	Oil tools, pumps, valves
Hardide-H Ultra-Hard	3000 – 3500 Hv	Satisfactory	8-12 µm	Self-sharpening blades
Hardide-M Multi-Layer	1600 – 2000 Hv	Good	Up to 40 µm	Erosion-resistance

3. Structure and Key Properties of Hardide Coating.

3.1. Micro-Structure of Hardide Coatings.

All Hardide coatings are crystallized from the gas phase as a result of a series of surface chemical reactions, with some of the intermediary reaction products having high mobility on the surface. This works as a “self-leveling” mechanism when any micro-pores and defects in the growing coating layer are filled, as a result producing exceptionally dense and pore-free layer. The porosity measured as the difference between theoretical and actual material density is less than 0.04%, while the coating completely covers the substrate without any through pores starting from less than 1 micron thickness. The absence of through-porosity is further proven by the tests in aggressive media described in details below.

Fig.1 below shows a cross-section of Hardide coating on a hard-metal WC/Co substrate, the cross section etching revealed its porous and grainy structure, while Hardide coating remains dense and pore-free. This is typical for all variants of Hardide coating.

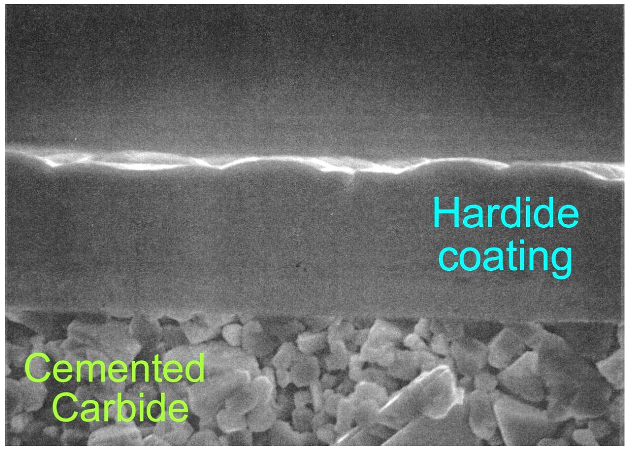

Fig.1 Electron Microscopy image of a cross-section of Hardide coating on WC/Co cemented carbide substrate. Etching exposes grainy structure of the substrate, while the coating is dense and pore-free.

3.2. Nano-Structure of Hardide-T.

Hardide-T is a nano-structured material which consists of a metallic tungsten matrix with dispersed tungsten carbide nano-particles typically between 1 and 10 nanometers in size. Fig. 2 presents a high resolution electron microscopy image of Hardide-T showing a Tungsten Carbide inclusion of 1-2 nanometers.

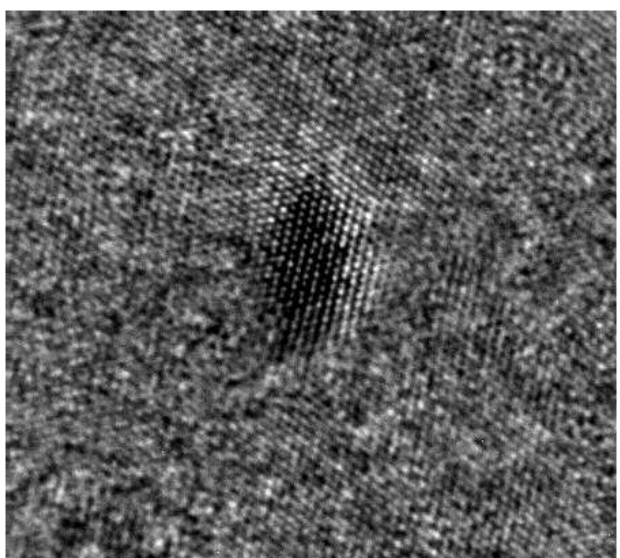

Fig.2. HREM micrograph of precipitate in Hardide-T deposited on copper substrate. The atomic distances (1.49 and 1.76Å) directly taken from the precipitate region are matched best to the lattice constants of W_2C (110- 1.49 Å and 102 – 1.74 Å). (The micrograph was produced at the Oxford University Department of Materials)

3.3. Hardness and Wear Resistance.

Hardness of pure metal Tungsten is approximately 350 Hv. The dispersed Tungsten Carbide nano-particles give Hardide-T significantly higher hardness which can be controlled and tailored to give a typical range of hardness of between 1100 and 1600Hv, and with other types of Hardide™ coating up to 3500Hv – that exceeds hardness of traditional pure Tungsten Carbide WC made by reaction between tungsten and carbon.

Hardness, wear and abrasion resistance are the key characteristics of Hardide-T important for valve applications, these properties have been extensively tested in the laboratory and proven in industrial environments. Fig. 3 presents the results of abrasion resistance tests performed in accordance with the ASTM G65 standard - Procedures A and B [5]. The results showed that the Hardide™ wear rate is 40 times lower than abrasion resistant steel AR-500, 12 times lower than Hard Chrome and four times lower than thermal spray WC.

Erosion resistance tests were performed in accordance with ASTM G76-95; velocity was 70 m/sec and aluminum oxide (particle size 50 µm) was used as the erosive material. Angles of impact for erosion tests were 90°, 60°, 45° and 30°. Hardide's erosion rate was 0.017 - 0.019 mm^3/g , which again is significantly better than the erosion rate of the tested types of cemented carbide, white iron, hard chrome and chrome carbide weld overlay. Hardide™ resists erosion by Alumina particles at 70 m/sec three times better than steel and more than two times better than cemented carbide (hardmetal). Hardide™ also significantly outperformed various currently used hard materials in a sand/water erosion test.

Hardide-T wear and erosion resistance are superior to the tested materials despite the fact that some of them have higher hardness. This enhanced performance of Hardide-T can be explained by its excellent toughness and fatigue resistance. Micro-cracking and chipping are the main mechanisms of wear and erosion of hard materials like flame-spray Tungsten Carbide or Hard Chrome. A tougher material will resist this degradation better.

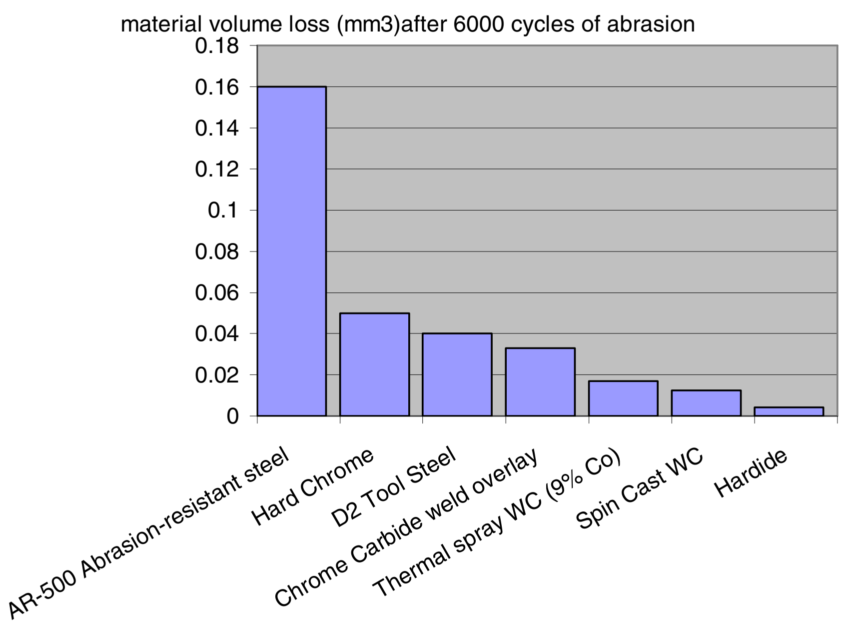

Fig. 3. Results of ASTM G65 tests of Hardide coating abrasion resistance as compared to the results for other hard materials.

3.4. Ability to coat internal surfaces and complex shapes

Hardide™ coatings are deposited by Chemical Vapour Deposition (CVD) technology from the gas phase. This allows uniform coating of complex shapes and internal surfaces which is important for applications with parts like balls, complex shape seats, pump cylinders and actuator threads. Fig.4 below illustrates this as it shows a cross-section of thread coated with 50-microns thick Hardide, which follows and repeats accurately even small imperfections in the substrate. Most other coating technologies either are not able to coat internal surfaces (HVOF spray, D-gun), or cause thicker coating build-up on sharp edges (hard Chrome). Ability of Hardide™ to coat shaped and internal surfaces opens new possibilities for design.

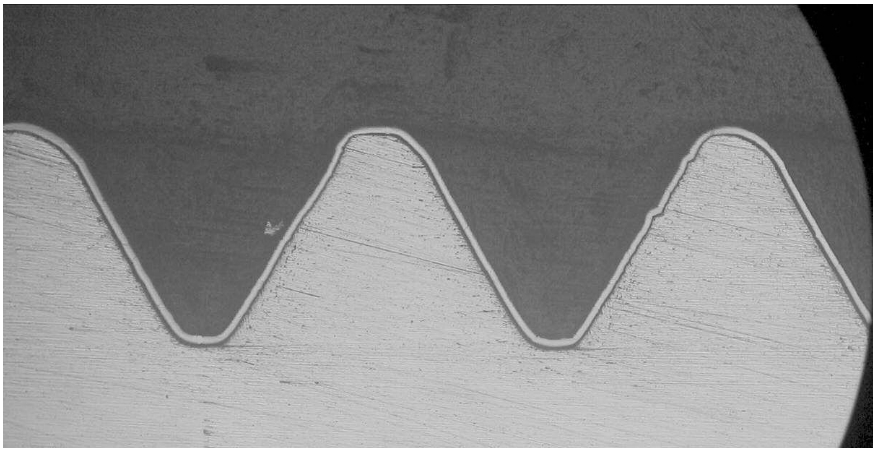

Fig.4. A micro-photograph of a cross-section of 50-microns thick Hardide-T coating on thread. The uniform coating follows the substrate; even slight imperfections are accurately followed.

3.5. Protection against aggressive media

Unlike sprayed Tungsten Carbide, Hardide does not use Cobalt which can be affected by acids; this is especially important for processing sour oil. Hardide™ was tested by Bodycote Materials Testing for resistance to aggressive media in accordance with the NACE Sulphide Stress Cracking test in a solution of 5% NaCl, 0.5% Acetic acid, saturated with H_2S [9]. Stainless steel 17-4 and 316 and Inconel 625 samples coated with Hardide™ were tested in deformed conditions of up to 3000 microstrain.

Fig.5 shows two samples of 17-4 PH stainless steel after the 30-days test: the top dark plate is a control uncoated sample which cracked across the full 20 mm width and shown extensive micro-cracking and pitting. The bottom, lighter sample was coated with Hardide and shown no cracking or degradation after the same test.

Fig.5. Uncoated (top) and Hardide-coated (bottom) samples of 17-4 PH stainless steel after 30 days Sulphide stress cracking test (photograph from Bodycote report [9]).

Due to its deposition mechanism, Hardide™ is free from through porosity from a thickness of less than 1 micron. Pore-free coatings have high chemical resistance and protect the substrate from attacks by aggressive media. Traditionally used coatings like flame-spray or Hard Chrome have micro-pores and micro-cracks which open when the substrate deforms under load and allow the solution to attack the substrate.

Fig. 6. Pore-free Hardide™ coating protects the substrate against aggressive media attacks; a micro-graph of a Hardide-coated sample of 17-4 stainless steel after 30 days in solution of NaCl, Acetic Acid and H2S (micro-photograph from Bodycote report [9]) .

Chemical resistance of Hardide was further tested when a sample made of 4140 steel and coated all over with Hardide-T was completely immersed in uninhibited 28% HCl for 24 hours. There was no visible effect of the acid on the coating and no weight loss occurred. Any micro-pores in coating will result in acid attacking the substrate and creating “blisters” by lifting the coating – as often observed with porous sprayed coatings.

3.6. Toughness and Flexibility of Hardide Coating.

Toughness and impact resistance are essential for practical applications as some degree of shock load is likely to happen when for example a down-hole tool is moved inside an oil well. Among thick coatings Hardide™ has exceptional toughness and impact resistance, this was an important enabling factor for a number of applications. Hardide™ can be applied as a tougher substitute to brittle cemented carbide WC/Co for parts suffering from impact. One of Hardide's customers – a producer of valves for the oil and gas industry - developed a valve seat which deformed in operation. Traditional coatings like HVOF spray are not suitable as they crack or chip under this deformation. Hardide is proven to withstand deformations of 3000 microstrain without micro-cracking and has now been tested and approved for this application. This confirmed the theoretical expectation that nano-structured materials can show unique toughness, crack and impact-resistance.

Fig. 7 and 8 below show examples of Hardide coating deformations by impacts and "hammer testing", in both cases no flaking, cracking or spalling of coating occurred. NACE corrosion tests were performed with coated samples deformations which would crack most of the currently used hard coatings, meanwhile absence of micro-pores in Hardide was proven by the fact that the substrate material was not attacked by the aggressive media.

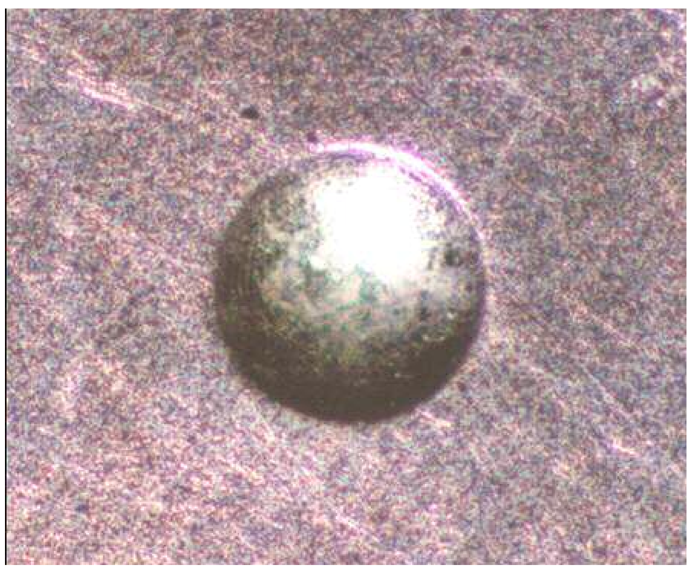

Fig.7. Micro-photo of a crater made by a ball impact into 50 microns thick Hardide-T coating on steel. Ball diameter 1 mm. Absence of cracking, chipping or spalling demonstrate coating's unique toughness and flexibility.

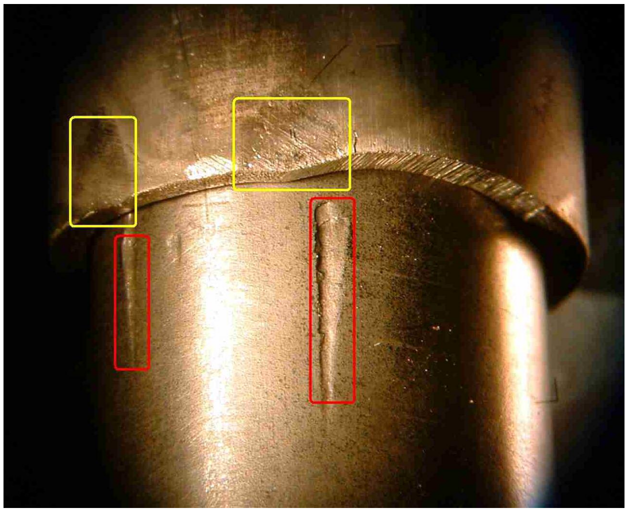

Fig.8 Hardide-coated Inconel pin and Monel bush survived intense repeated hammer impacts without fracture or flaking

3.7. Anti-galling properties

Hardide-T also possesses excellent anti-galling properties. As Tungsten and Tungsten Carbide are both high melting point materials (Tungsten's melting temperature is the highest among metals at 3387°C) they will not micro-weld to another Tungsten-based surface or other metals, thereby eliminating the cause of galling. As a result Hardide has shown excellent anti-galling properties when tested on a screw actuator. As the coating is hard and wear resistant, this anti-galling treatment will be durable in an abrasive environment.

Hardide-T will replicate the 'as supplied' customer component surface finish and in the majority of cases no post-coat machining is required. The 'as coated' surface finish provides a nodular but smooth surface texture. The coating also reduces the wear of other uncoated materials which are working in contact with Hardide-T e.g. elastomeric seals last longer when working against Hardide-T compared to the same seals working against stainless steel due to the uniform structure of the coating, its chemical inertness and low friction.

4. Applications of Hardide-T Coating.

Hardide™ has proven as an enabling material for a broad variety of applications with components operating in abrasive and erosive environments, including critical components of downhole tools used in the oil and gas industry, and pumps handling abrasive fluids such as paints. The demand for Hardide™ with valve applications is growing very quickly due to the material's unique combination of properties: wear and erosion resistance, non-porous structure and anti-galling properties. In other sectors, it is being used in the power, chemical and food manufacturing industries and in aerospace by BAE Systems on the Eurofighter Typhoon.

4.1. Down-Hole Tools for Oil and Gas Industries.

In a drilling tool application for one of the largest global oilfield services providers, the coating has increased the life of critical components three-fold. The components were operating in an extremely abrasive environment and typically failed after 60 hours due to excessive wear. After being coated with Hardide-T, the life of the parts was proven, in the lab and the field, to extend to more than 200 hours. This has enabled uninterrupted drilling for far greater periods of time and the savings in down-time and tooling costs are significant. Most of this customer's tools are now in use with Hardide-coated parts. Hardide-T appeared to be the only available solution for this application as traditional hard materials were too brittle and difficult to machine due to the complex part geometry, while other coating technologies were not able to reach the important hidden surface areas.

The coating is particularly suitable as a wear protective coating in applications requiring shock-resistance. Testing is at an advanced stage for Hardide-coated bushes for a drilling tool in such an application. As the bushes, which bear a rotating pin, have to resist abrasion in drilling mud, they are currently made of cemented carbide. In the event of a shock load however, they shatter and cause tool failure. In lab tests carried out by a global oilfield services company, Hardide-coated Inconel bushes have proven "indestructible" when their abrasion and shock resistance is "hammer tested". In this case, the ability of Hardide-T to coat internal surfaces was another enabling factor as it is the inside of the bush that suffers from abrasion and wear and this is where other coating technologies cannot be applied.

4.2. Applications with Valves.

Ball valves similar to those shown on Fig.9 will suffer from abrasion by sand or stone chippings present in the fluids or from erosion by accelerating flow when the valve is being closed/opened. Hardide™ coatings make the valve parts scratch-proof and able to resist abrasion and erosion. This significantly increases the valve life.

LG Ball Valves Ltd, a UK producer of ball valves is a Hardide customer which started using the coating in 2003. Most of the Hardide-coated LG Ball Valves' valves are used in topside applications in the oil and gas industry – these are in service in the UK, Norway and South Africa as well as in high pressure oil refinery applications. The Hardide-coated valves have been in service for between one and two years with no failures reported.

In an instant coffee manufacturing application, Hard Chrome plated ball valves suffered from intensive abrasion and erosion and had to be replaced every few days. Since being Hardide-coated, they have been in continuous service for over 18 months.

Hardide-coated LG Ball Valves' valves are also used successfully in specialty chemicals manufacturing where chemical resistance is required. In these cases, the coated valves have been in service for more than six months while previously the valves were failing every few days or weeks. Hardide-coated valves are also in use in cryogenic equipment controlling liquid Helium at temperature of -196oC and pressure 200 bar; an application which is very abrasive for valves.

The zero porosity of Hardide-T is important for applications with valves where any porosity can result in gas diffusion through the coating layer leading to a potentially explosive mixture. For this reason, spray coatings are often sealed with polymeric materials to close surface porosity but this limits their operation temperature. This sealing would still leave unsealed pores deeper in the coating layer which may open in use later. Hardide-T is produced pore-free across the whole thickness of the coating layer. The coating is used commercially on valves in the oil and gas, food manufacturing, chemical industries and cryogenics at liquid Helium temperatures. In the food and chemical sectors, the use of Hardide-T has solved problems for customers where the combination of abrasive and chemically aggressive environments was causing valve failure every few days. Hardide-coated valves have now been in continuous operation in both applications for more than six months without failures.

Fig.9. Ball valves coated with Hardide™.

Hardide™ solves another practical problem for producers of valves with complex shaped components. If a spray coating is applied to such parts they have to be machined to restore the shape after coating. This can be a very complicated and expensive operation in some cases even practically impossible due to the complex shape, which limits such coatings applications. Hardide™ coating, as applied, is very smooth and uniform; coated valve parts usually require only polishing to achieve a finish of typically 0.3 microns Ra. This vastly streamlines finishing operations, especially for complex shaped parts. Ease of finishing, ability to coat complex shapes uniformly and Hardide's unique flexibility therefore enables new valve designs where traditional brittle hard coatings and materials cannot be used.

4.3. Applications with Pumps.

Hardide-T is successfully used to extend life of positive displacement pumps handling viscous fluids such as paints. Pigments and various special paint additives like Alumina or glass beads are highly abrasive and wear out pumps quickly. Hardide-T coating has been applied to both pump piston outside surface and cylinder inside, which increased the pump life in average by factor of 4. Ability to coat internal surfaces and complex shapes was essential for this application. The pumps use elastomeric seals and packing, these seals previously suffered intensive wear if traditional hard coatings were used. Hardide-T in fact reduced the wear of the seals, that reduces the pump maintenance requirements.

4.4. Replacement of Hard Chrome.

Hardide offers an attractive substitute to Hard Chrome which has to be phased out due to environmental issues. Hard Chrome is still widely used in many applications in aerospace, mining, tooling industries, mainly because it provided a combination of protective properties against wear and corrosion and there was no suitable replacement available having similar properties [10]. Table 2 below lists key requirements to an effective Chrome substitute formulated in [10], as well as Hardide characteristics – which in most positions improve what Hard Chrome can offer.

HVOF spray coating is currently considered the most suitable replacement of Hard Chrome, meanwhile a major limitation of HVOF technology is that it can not coat internal surfaces where the spray head wouldnot fit. HVOF is also not efficient for coating small parts and complex shapes, this coating as deposited is very rough and have to be ground finished, that is a complex and expensive operation because of the coating hardness.

This makes Hardide a particularly attractive Hard Cr replacement for internals and small parts, parts with complex shapes where good finish is required.

Table 2. Hardide as Hard Chrome Replacement (uses data from Keith Legg, Rowan Technology Group TSSEA Spring Conference April 20, 2005)

Property	Hard Chrome	Hardide
Hardness	800 – 1,000 HV	1,100 – 3,500 HV
Friction	Low metal-to-metal	Typically between 0.2 and 0.5
Corrosion	Poor (cracked) unless Ni underlay or polymer sealer	Very good resistance to acids and aggressive chemicals
Fatigue	Significant fatigue debit	Compressive stresses are favourable
Hydrogen embrittlement	High – needs 375F for 23 hours	Vacuum process
Stripping	H_2SO_4	Can be done by proprietary method
Finishing	Al_2O_3 wheel grind to 8 micro-inch Ra typ.	Can be polished, ground, honed to very good finish

5. Summary and Conclusions

The nano-structured Hardide-T coating is an advanced material which offers a unique combination of protective properties, including ultra-hardness, wear and erosion resistance as well as toughness, impact and crack resistance. These properties make Hardide an "enabling material" for advanced mechanical systems, especially those operating in abrasive/erosive environment, suffering from impact or shock loads, deformations and in aggressive media. The use of Hardide opens new opportunities for the design of valves.

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